



Influence of water vapour on plasma/photocatalytic oxidation efficiency of acetylene

F. Thevenet^{a,*}, O. Guaitella^b, E. Puzenat^c, C. Guillard^c, A. Rousseau^b

^a Département Chimie & Environnement, Ecole des Mines de Douai, 941 rue Bourseul, 59508 Douai, France

^b LPTP Laboratoire de Physique et Technologie des Plasmas, UMR CNRS-Ecole Polytechnique, 91120 Palaiseau, France

^c IRCELYON, UMR CNRS-Université Lyon-1, 2 Av. A. Einstein, 69626 Villeurbanne, France

ARTICLE INFO

Article history:

Received 24 April 2008

Received in revised form 11 June 2008

Accepted 18 June 2008

Available online 15 July 2008

Keyword:

Non-thermal plasma

ABSTRACT

Non-thermal plasma as well as photocatalysis is intensively investigated for volatile organic compounds (VOCs) oxidation. Their association exhibits high performances for air pollutant removal and mineralization. Nevertheless, numerous experimental investigations are performed under dry conditions, or on very short range of water vapour amounts. This article aims at determining the influence of water vapour on the oxidation efficiency of (i) photocatalysis, (ii) non-thermal plasma, and (iii) their association. The amount of water vapour investigated in dry conditions ranges from 0 ppm to 23,000 ppm. Acetylene has been selected as a model pollutant. The presence of water vapour in the gas stream induces a strong decrease in the photocatalytic oxidation of acetylene. The mineralization process is modified. The efficiency of acetylene removal by non-thermal plasma decreases regularly with the water vapour amount. Nevertheless, the presence of water vapour improves significantly the selectivity of carbon dioxide. The same tendency is reported for plasma/photocatalysis association. Those results are interpreted in terms of oxidative species modification due to the presence of water. Moreover, the investigation of water vapour contribution into oxidative processes improves the understanding of plasma/photocatalytic association mechanisms.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Air treatment is mainly devoted to the removal of toxic, odorous or irritating volatile organic compounds (VOCs). Various techniques have been developed during the last 20 years to adsorb and/or to decompose molecules. First developed for water depollution [1], photocatalysis has been intensively studied for gas phase purification [2]. It consists in the activation of a semiconductor material, typically titanium dioxide, under UV radiations, in order to generate oxidative species. Saturated [3], unsaturated [4–6], or oxygenated [7,8] volatile organic compounds are sensitive to the advanced oxidation of irradiated TiO₂. Even compounds containing triple carbon–carbon bond, like acetylene [9], can be mineralized into carbon dioxide. In parallel, processes related to dielectric barrier discharge (DBD) have been developed for VOCs oxidation [10,11]. Authors report that non-thermal plasma is a very efficient process for numerous organic compounds removal from gaseous phase [12]. It is characterized by (i) a faster kinetics than photocatalytic process [13], (ii) the

formation of numerous organic intermediates or by-products. In order to take part of each technique and to evidence synergy between them, several authors coupled non-thermal plasma and catalytic [14] or photocatalytic [13] materials.

Studies are mainly focused on the fundamental understanding of the interaction phenomena between non-thermal plasma and photocatalysis. Consequently, reactions are performed under simplified conditions like synthetic dry air. Few works investigate water vapour as a chemical parameter. If experiments are performed in the presence of water vapour, H₂O concentration range is unfortunately short or reduced to one concentration. Nevertheless, real effluents contain water vapour, with fluctuating concentration. The presence of water vapour into the non-thermal plasma or the photocatalytic reactor can considerably modify its performances. It can give crucial pieces of information concerning plasma/photocatalytic association. In order to drive experimental conditions towards reality, and to improve fundamental knowledge of coupling systems, it is interesting to investigate the influence of water vapour on acetylene oxidation by non-thermal plasma and/or photocatalysis.

The influence of water vapour on gas phase photocatalytic oxidation is extremely different according to: (i) the compound to be oxidized, (ii) the morphology of the photocatalyst, and (iii) the

* Corresponding author.

E-mail address: thevenet@ensm-douai.fr (F. Thevenet).

amount of water vapour. Zhao and Yang [15] report that titanium dioxide surface is covered of physisorbed water molecules and hydroxyl radicals created by dissociative chemisorptions of water on the irradiated semi-conductor. Titanium dioxide wettability is considerably increased as the material is irradiated [16–18]. Kataoka et al. [19] have shown by transmission infrared spectroscopy the photopromoted adsorption of HO* radicals on irradiated titanium dioxide surface. In the absence of water vapour in the gas flow, the photocatalytic degradation of various compounds is delayed, and the complete conversion into CO₂ can be impossible. That is the case of toluene as reported by Guo et al. [20]. However, an excess of water vapour induces titanium dioxide surface coverage by hydroxyl groups. Active sites of the material are occupied and the catalytic activity consequently decreases [20]. The article of Raillard et al. [21] gives a good outlook of the complexity and the various effects of water vapour on the photocatalytic degradation of VOCs. They reported that the degradation rate of methylethylketone is not modified if water vapour does not exceed 2 g m⁻³. Indeed, in spite of numerous hydroxyl radicals on active sites, their presence favours the oxidation of the volatile organic compounds. Beyond this value, the effect of water vapour differs with the morphology of the photocatalyst: thin film vs. powder [21]. In the case of a powdered photocatalyst, competitive adsorption, between HO* radicals and the compound to be removed, disfavours the oxidative reaction. In the case of photocatalytic thin films, the formation of a thin layer of water molecules on material surface enables the solubilisation of the compound, improving the interaction with the photocatalyst.

The presence of water molecules in the gas stream flowing between dielectric barrier discharge electrodes leads to the formation of HO* and H* radicals because of the high electronic dissociative attachment coefficient of H₂O molecules [22]. The concentration of HO* radical that downstreams the reactor is proportional to the plasma input power, and their decay time is linked to the oxygen concentration in the gas stream [23]. Under pure nitrogen atmosphere the decay time is almost 100 ms, if 20% of oxygen is introduced in the flow, the value decreases to 100 μs [24]. Such a difference is explained by the high reactivity of HO* radicals with the species O(¹D), O₃ and O* generated from O₂ by the plasma. Consequently, in the presence of water, the composition and the reactivity of the plasma oxidative phase is considerably modified, HO* tends to become the main oxidative species.

2. Experimental

The same reactor has been used for photocatalytic, non-thermal plasma and coupling experiments in order to enable comparisons. It consists in a Pyrex planar double dielectric barrier discharge (gap: 8 mm; width: 8 cm; length: 2 cm). As non-thermal plasma experiments are performed, the discharge is ignited by a 50-Hz sinusoidal power supply (Fig. 1). The Pyrex walls of the reactor are used as dielectrics. The maximum operating voltage is 27 kV. Electrodes are made of thin copper sheets stuck on each dielectric outer surface. The input power of the discharge was determined by Lissajous plot [25]. Calculations based on Manley model [26] have been developed to determine

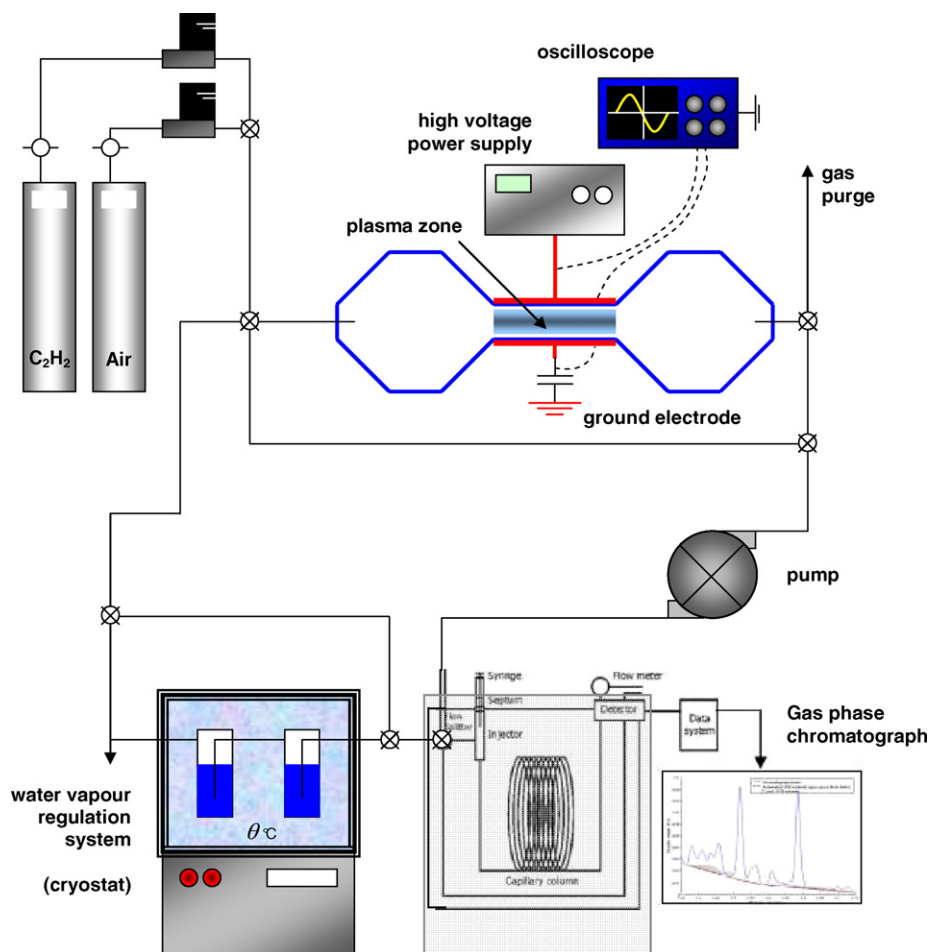


Fig. 1. Plasma/photocatalysis coupling setup equipped with water vapour regulating system and GC-methanizer-FID analytical device.

the effective input power [27]. Voltages were measured using Lecroy high voltage probes. Signals were monitored with Lecroy WaveSurfer oscilloscope. Experiments were performed under 0.2 W plasmas. The applied voltage adjustment enables input power regulation. As photocatalytic experiments are performed, the photocatalytic material is placed inside the reactor, on the lower inner wall of the device so that streamer filaments spread on material surface. External UV-illumination is laterally performed by four PLL40-Philips UV lamps.

The coupling material consists in glass fibres coated with 20 g m^{-2} of colloidal silica, ensuring the deposition of 20 g m^{-2} of P25-Degussa titanium dioxide nanoparticles (material named: Si20Ti20), this material is photocatalytically active. The photocatalyst has been prepared by Ahlstrom Research and Services. The coating process consists in an impregnation of glass fibres by SiO_2 and TiO_2 nanoparticles suspension in pure water using Ahlstrom industrial size-press. Specific surface areas have been measured according to BET method: Si20Ti20 is $20.6 \text{ m}^2 \text{ g}^{-1}$. Materials consist in 2 mm thick sheets of woven fibres. Sheets can be cut into rectangular pieces (8 cm long, 2 cm wide). Those pieces are placed on the dielectric covering the lower electrode of the discharge. The presence of material affects the discharge ignition and the input power. For example the discharge breakdown is lowered by 1000–1500 V in the presence of fibres. At the beginning of each experiment, the voltage is adjusted so that reactions are performed at the desired specific energy.

Experiments have been performed in a recirculation mode, meaning that the same gas batch is treated during the experiment. Recirculation is ensured by a pump placed on the gas circuit. Gases used for experiments were all provided by Air Liquide. First, the reactor and the gas circuit are purged with 200 mL/min synthetic dry air for 12 h. Then the circuit is closed and the pump is switched on, it enables a 200 mL/min recirculation flow. At the beginning, bubblers containing high purity water placed inside the cryostat are part of the circuit. The amount of water vapour in the outlet gas flow is regulated by the temperature of the bath. The explored temperature range goes from 5 to 20 °C. The corresponding amount of water vapour ranges from 8600 to 23,000 ppm. Experiments have been performed with an amount of 4300 ppm of water vapour by mixing humid air from bubblers thermostated at 5 °C with dry air. The introduction of water vapour in the gas stream is performed for 3 h so that the reactor and the photocatalyst get stabilized. Then the water vapour regulation system is by-passed and the batch is recirculated by the pump. Pure acetylene is introduced inside the reactor with a micro-syringe so that acetylene concentration reaches 3000 ppm. After a one-hour homogenization under recirculation, UV lamps are switched on.

C_2H_2 , CO and CO_2 were monitored using Varian gas phase chromatograph. The system was especially developed for those experiments. It makes possible the simultaneous elution and analysis of VOCs as well as carbon monoxide and dioxide. A 25-m long Carbobond capillary column has been employed. C_2H_2 is detected by flame ionization (FID), whereas CO and CO_2 are first converted into methane over Ni catalyst under hydrogen flow and then detected by FID.

Adsorbed acids on porous Si20Ti20 solid placed inside the discharge during photocatalytic experiments were analyzed by high precision liquid chromatography (HPLC). It consists in a Varian ProStar device equipped with Sarsep-car-H packed column to perform acids separation. Detection was ensured by UV absorption at 210 nm. First, a one-hour extraction, including five minutes sonication, was performed on Si20Ti20. The extraction solution consists in a pH 2 H_2SO_4 aqueous solution equivalent to HPLC device eluent. This procedure was character-

ized by first extraction coefficient ranging from 92 to 97% for all acids considered.

3. Results

In order to enable the understanding of water vapour influence on acetylene removal by non-thermal plasma and photocatalysis, each oxidative configuration has been investigated separately: (i) influence of water vapour on acetylene photocatalytic oxidation; (ii) influence of water vapour on acetylene non-thermal plasma oxidation; finally, regarding to those results (iii) the influence of water vapour on the “non-thermal plasma/ TiO_2 ” coupling oxidative system is discussed. The influence of UV irradiation added on the coupling oxidative system is reported too.

3.1. Influence of water vapour on acetylene photocatalytic oxidation

The removal of acetylene on irradiated photocatalytic material Si20Ti20 has been performed in the presence of various water vapour amounts. After each experiment the removal rate of acetylene has been calculated, values are reported in Fig. 2 as a function of water vapour amount expressed in ppm.

Under dry air, the removal rate of acetylene is 27 ppm/min, it decreases to 16 ppm/min, 10 ppm/min and 8.5 ppm/min when the amount of water vapour respectively increases to 4000 ppm, 8000 ppm and 10,000 ppm. The presence of water vapour in the reactor induces a significant and regular removal rate and decreases even at low concentration. Above 12,000 ppm, an increase of water vapour amount does not modify acetylene removal rate, a stationary state seems to be reached at 8 ppm/min. The decrease of the photocatalytic is noticeable in Figs. 3 and 4 too. Those figures report CO_2 and CO formation rates as a function of water vapour quantity.

Initial formation rate of carbon dioxide, like acetylene initial removal rate, decreases regularly as water vapour amount increases till 10,000 ppm. Under dry air, the initial formation rate of carbon dioxide is 47 ppm/min, it decreases to 22 ppm/min and 9 ppm/min respectively in the presence of 4000 ppm and 10,000 ppm of water vapour. Beyond 10,000 ppm of water vapour, a stationary state is established at 7 ppm/min. Carbon monoxide formation rate is stable since water vapour remains below 10,000 ppm. On this range carbon monoxide formation rate is 2.2 ppm/min in average. Beyond 10,000 ppm, CO formation rate collapses to 0.2 ppm/min and remains stable at this value.

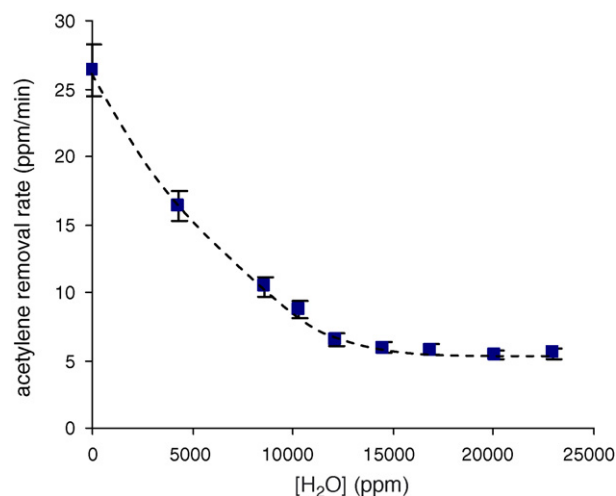


Fig. 2. Evolution of acetylene removal rate by photocatalytic process as a function of water vapour amount expressed in ppm.

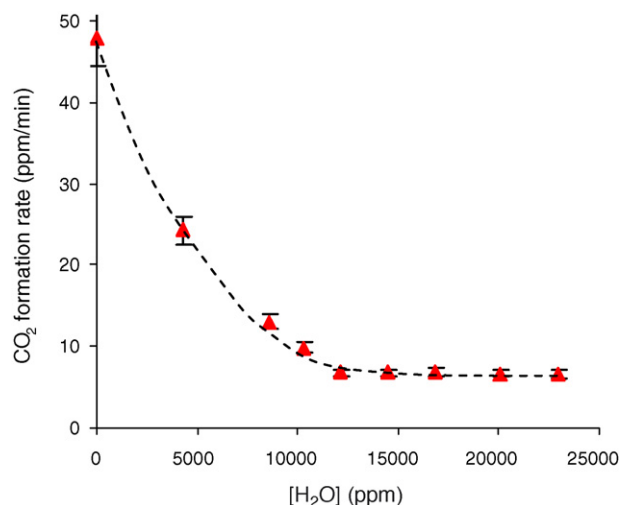


Fig. 3. Evolution of carbon dioxide formation rate during photocatalytic oxidation of acetylene as a function of water vapour amount expressed in ppm.

The presence of water vapour into the reactor obviously slows down the oxidation reaction kinetics. Under our conditions, the inhibiting effect of water vapour is already noticed at the lowest amounts. We suggest that a competitive adsorption between water and acetylene occurs, and this phenomenon would not be balanced by the reaction of hydroxyl radicals on acetylene. HO[•] radicals are produced by the reaction of photogenerated holes with water. The activity decrease reveals that acetylene mainly reacts with photo-generated holes. Reaction constants available on NIST kinetics database confirm that acetylene mainly reacts with O[•] ($k_{(O^{\bullet})} = 10^{-11} \text{ cm}^3/\text{mol s}$) in comparison to HO[•] ($k_{(HO^{\bullet})} = 10^{-13} \text{ cm}^3/\text{mol s}$).

The decrease of CO₂ and CO formation rates is coherent with the decrease of C₂H₂ removal rate. Nevertheless, the precise comparison of rates calculated under dry air or in the presence of 15,000 ppm of water exhibits another phenomenon: CO₂ formation rate is divided by 7 whereas acetylene removal rate is only divided by 4.8. Under dry air, acetylene conversion into carbon dioxide was completed and instantaneous [9], which is not the case in the presence of water vapour, meaning that reaction intermediates are favoured. Fig. 5 reports: (a) the concentration profiles of C₂H₂, CO₂, CO as a function of the irradiation time performed

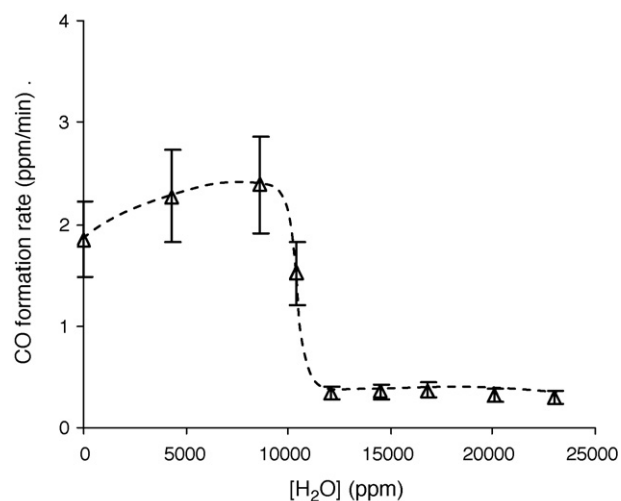


Fig. 4. Evolution of carbon monoxide formation rate during photocatalytic oxidation of acetylene as a function of water vapour amount expressed in ppm.

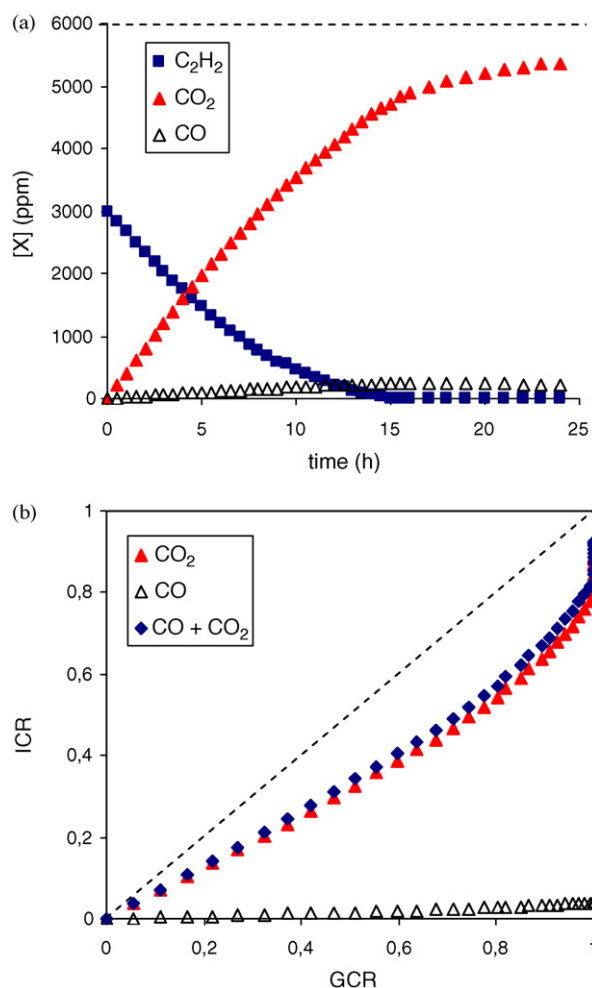


Fig. 5. Photocatalytic oxidation of acetylene performed in the presence of 20,000 ppm of water vapour: (a) evolution of C₂H₂, CO₂ and CO concentrations as a function of time; (b) evolution of intermediates conversion rate (ICR) as a function of global conversion rate (GCR) calculated for CO₂, CO, and their sum.

with 20,000 of water vapour; (b) ICR/GCR plot of CO, CO₂ and their sum under the same conditions. An ICR/GCR graphic corresponds to the plot of intermediate conversion rates as a function of the global conversion rates of the initial compound. The closer the data fit the diagonal line, the faster the mineralization occurs. Under dry conditions, the data fitted the diagonal line [9], which is not the case under wet conditions; a significant gap is noticeable in Fig. 5b between the CO + CO₂ sum and the diagonal line. The carbon balance is not completed since the beginning of the reaction. As 80% of acetylene is removed, more than 20% of the carbon balance is missing. Nevertheless, the formation of CO and CO₂ still occurs as acetylene is completely removed. The presence of water vapour improves the formation of reaction intermediates; the mineralization of acetylene is only delayed.

Si20Ti20 photocatalyst has been collected from the reactor after 10 h of acetylene oxidation in the presence of 20,000 ppm of water vapour. After extraction and HPLC analyses, three carboxylic acids have been identified: formic acid, acetic acid, and oxalic acid. Those acids were the same formerly evidenced under dry conditions. Moreover, their relative abundances are similar in the presence of water vapour and under dry air. This behaviour suggests that water vapour would not modify significantly the photocatalytic reaction pathway, but strongly slows down the kinetics. Indeed, according to NIST kinetics database, reaction constants of acetic acid and

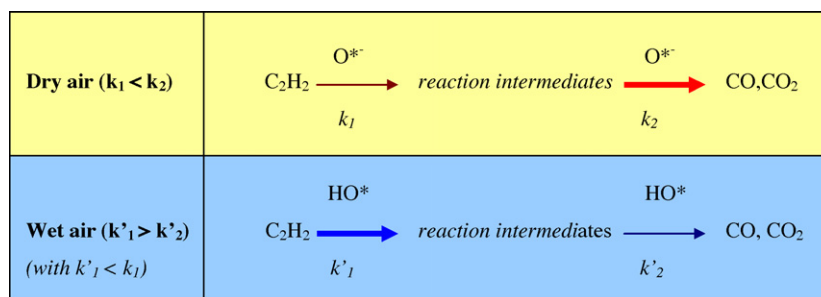


Fig. 6. Kinetics scheme of the difference between photocatalytic oxidation of acetylene under dry and wet air.

formic acid with O^* are $10^{-10} \text{ cm}^3/\text{mol s}$. Consequently, under dry air, since O^* is the main oxidative species the limiting step of the process is the oxidation of acetylene. Reaction intermediates react faster and do not accumulate on the photocatalyst surface. On the contrary, reaction constants of acetic acid and formic acid with HO^* are one or two order of magnitude inferior to the reaction constant of acetylene with HO^* . Since HO^* becomes the main oxidative species, under wet conditions the limiting step is the oxidation of reaction intermediates which accumulate. We noticed indeed that the amount of carboxylic acids is multiplied by 9 under wet air in comparison to dry air. The kinetic modifications induced by water vapour is summarized in Fig. 6.

3.2. Influence of water vapour on acetylene oxidation by non-thermal plasma

Acetylene removal and CO_2/CO formation have been monitored for various amounts of water vapour; each experiment being performed under 0.2 W plasma. Adjustment of the input power was necessary since the composition of the atmosphere (dry or wet) markedly modifies the breakdown voltage and the energy deposition. Kinetic rates were calculated for each compound and condition. They have been plotted as a function of water vapour amount in Fig. 7.

The introduction of water vapour in the gas stream induces a regular decrease of acetylene removal rate on the whole studied range: from 190 ppm/min under dry air to 170 ppm/min in the presence of 23,000 ppm of water vapour. The decrease on the whole studied water vapour range represents 10.5% of the initial removal rate under dry air. Carbon monoxide formation rate is inhibited too by the presence of water vapour. The decrease on the whole studied water vapour range represents 45% of the initial formation rate under dry air (from 92 ppm/min under dry air to 50 ppm/min in the presence of 23,000 ppm of water vapour). On the contrary, the formation rate of CO_2 is clearly enhanced by the presence of water vapour. Under dry air the formation rate of carbon dioxide is 50 ppm/min, it increases to 67 ppm/min in the presence of 23,000 ppm of water vapour (+34%).

As reported by Guaitella et al. [28] O^* is a crucial oxidizing species of acetylene under dry plasma treatment. The disappearance of this species due to H_2O electron scavenging could explain the decreasing efficiency of plasma with an increasing H_2O amount. Atomic oxygen is mainly produced by electron impact on O_2 , nevertheless, H_2O is easily dissociated by electron impact into H^* and HO^* , inducing the decrease of available hot electron density. Experiments have been performed in order to confirm this hypothesis. The concentration of ozone is directly related to the density of O^* . Consequently, O_3 has been monitored by UV absorption spectroscopy under dry air and wet air (20,000 ppm H_2O). As reported in Fig. 8, the presence of H_2O divided by 4, the ozone concentration downstream the reactor. Since the formation

of O_3 is inhibited, it indicates that atomic oxygen amount is considerably reduced.

The decrease of CO formation rate and the increase of that of CO_2 with the amount of water molecules in the gas stream are reported by several authors with various interpretations. Ogata et al. [29] suggest that CO_2 and CO are produced by two different pathways, water would be supposed to favour the oxidation of the reaction intermediates leading to CO_2 and its action would disfavour the pathway to CO. This interpretation is poorly probable since even if different pathways exist, CO and CO_2 would be related by an equilibrium under plasma action as reported by Rudolph et al. [30]. Futamura and Yamamoto [22] take into account this equilibrium between CO and CO_2 and suggest that the presence of HO^* radicals shifts the equilibrium towards the formation of CO_2 . The improvement of carbon dioxide formation would be due to an improved oxidation of carbon monoxide, which is not in contradiction with an inhibition of acetylene removal.

Even if the presence of water vapour inhibits the removal of acetylene by non-thermal plasma, this inhibition is weak. More-

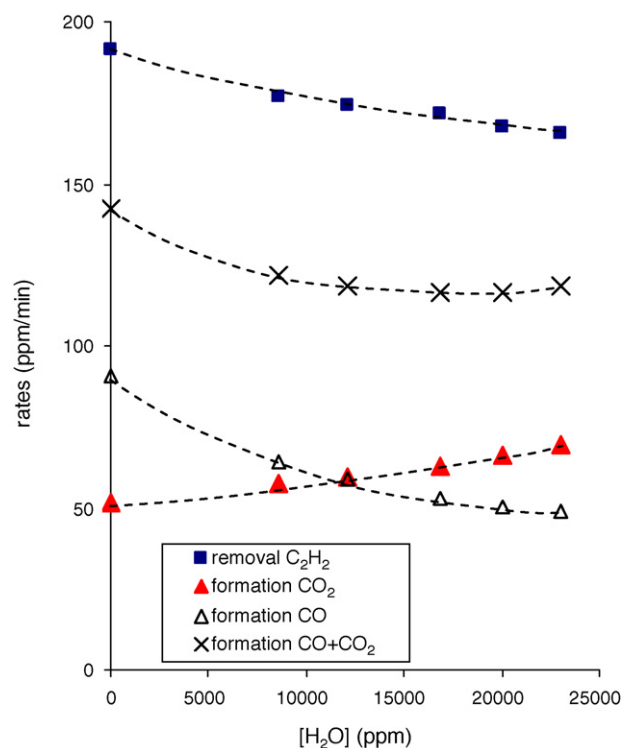


Fig. 7. Evolution of acetylene removal rate, carbon dioxide and carbon monoxide formation rates during non-thermal plasma oxidation of acetylene as a function of water vapour amount expressed in ppm.

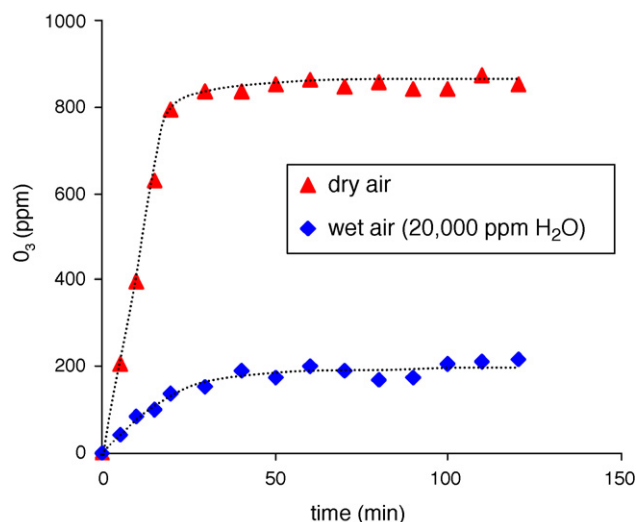


Fig. 8. Evolution of ozone amount generated by the dielectric barrier discharge device as a function of time in the recirculation mode under dry air and wet air (20,000 ppm of H₂O).

over, the formation of carbon monoxide is clearly reduced and the selectivity of carbon dioxide is highly improved.

3.3. Influence of water vapour on acetylene oxidation by non-thermal plasma coupled with a photocatalyst

3.3.1. Acetylene removal

Acetylene oxidation has been performed under two coupling conditions: (i) Si₂O₂Ti₂O photocatalyst is placed inside the discharge and the reactor remains in the dark (no irradiation by external UV lamps); (ii) Si₂O₂Ti₂O photocatalyst is placed inside the discharge and is irradiated by external UV lamps during the experiments. Each plasma experiment has been performed with an injected power adjusted to 0.2 W. Acetylene removal rates have been calculated for both coupling device in the presence of various amounts of water vapour, results are reported in Fig. 9. Former curves obtained by plasma treatment and photocatalytic treatment alone are reported in Fig. 9 too with dot-line to enable comparison.

In the absence of UV irradiation and under dry air, the presence of the porous photocatalyst inside the discharge improves acetylene removal rate by 12–14%. This improvement is noticed on the whole investigated range of water vapour amount. As stated in Section 3.2 water vapour modifies the plasma main oxidative species. The promotional effect related to the porous surface placed inside the discharge does not seem to be correlated to the nature of the main oxidative species.

In the presence of UV irradiation, acetylene removal rate is clearly enhanced in dry air. This effect decreases as water vapour amount increases in the reactor. Beyond 15,000 ppm of water, the efficiencies of both couplings are equivalent, UV irradiation becomes useless.

Ohtani et al. [31] and Pichat et al. [32] noticed that O₃ is possibly decomposed on irradiated titanium dioxide surface. Consequently, in dry air, plasma can improve the presence of O* and O₂⁻ species on TiO₂ surface. As reported in Section 3.2 water vapour reacts with O* and inhibits O₃ formation, mainly leading to the formation of HO* and HO₂*. In wet air, HO* radicals are mainly chemisorbed on titanium dioxide surface. Since TiO₂ photocatalyst generated holes are occupied by OH groups, and since acetylene poorly reacts with HO* (Section 3.1), the promotional effect of

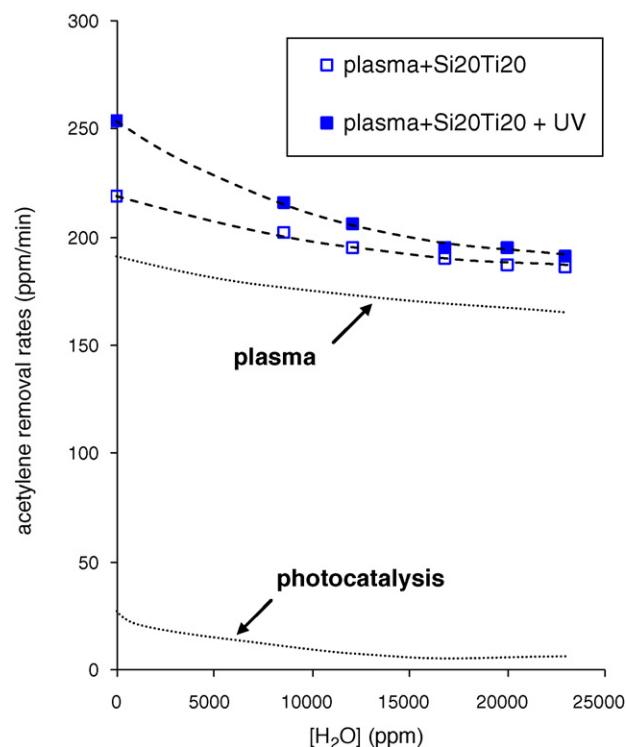


Fig. 9. Evolution of acetylene removal rate as a function of water vapour amount during acetylene oxidation by non-thermal plasma associated to Si₂O₂Ti₂O material, UV-irradiated or not. Former values obtained with plasma and photocatalytic treatments are reminded by dot-lines.

UV irradiation on coupling disappears in the presence of water vapour. This behaviour is coherent with the evolution of carbon dioxide formation rate during wet air photocatalytic oxidation of acetylene (Section 3.1). This phenomenon suggests that one main interaction between non-thermal plasma and photocatalysis is the influence of non-thermal plasma on the population of adsorbed species on irradiated titanium dioxide surface.

3.3.2. CO and CO₂ formation

Carbon dioxide and carbon monoxide formation rates are reported as a function of water vapour amount in the reactor for both coupling respectively in Figs. 10 and 11. Former curves obtained by plasma process and photocatalytic process are reported by dot-line to enable comparison on both figures.

In dry air, the presence of non-irradiated porous photocatalyst reduces by 23% the formation of carbon monoxide. This phenomenon is noticed on the whole studied range of water vapour. The illumination of the photocatalytic material with UV does not influence the formation rates of CO.

The behaviour of carbon dioxide formation rates is completely different. The presence of the porous material inside the discharge does not influence CO₂ formation rates. Under wet condition and in the presence of the porous material, the equilibrium between CO and CO₂ as described in Section 3.2 is still shifted towards CO₂ formation. UV irradiation strongly favours CO₂ formation in dry air, but this promotion is annihilated by the increase of water vapour, as noticed for acetylene. This phenomenon indicates that CO₂ selectivity enhancement by UV irradiation on coupling system is directly linked to a photocatalytic effect which is inhibited by water vapour as described in Section 3.3.1. Nevertheless, a minimum is noticed on CO₂ formation rate in the presence of 12,000 ppm of water. The inhibition of the UV-induced effect

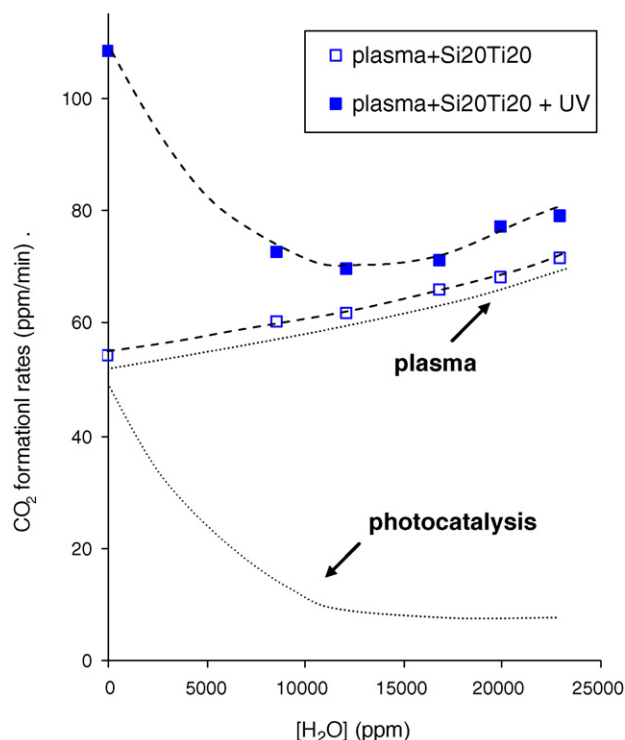


Fig. 10. Evolution of CO_2 formation rate as a function of water vapour amount during acetylene oxidation by non-thermal plasma associated to $\text{Si}_{20}\text{Ti}_{20}$ material, UV-irradiated or not. Former values obtained with plasma and photocatalytic treatments are recalled by dot-lines.

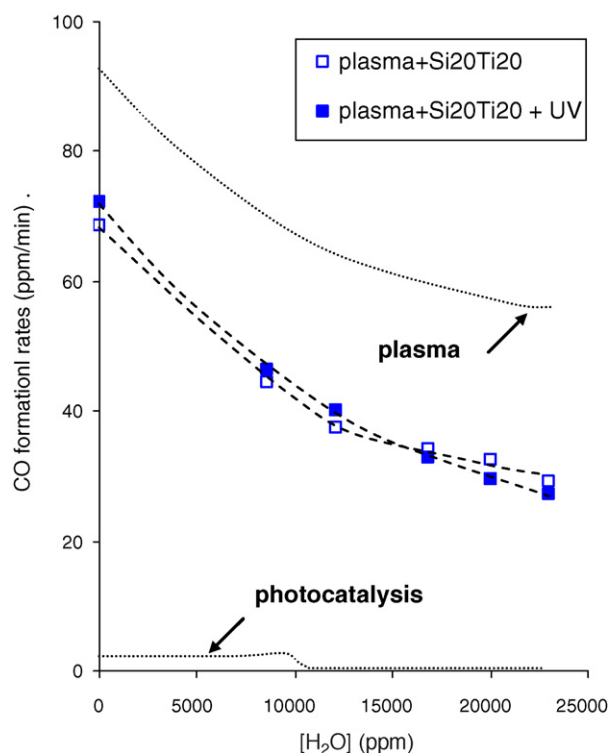


Fig. 11. Evolution of CO formation rate as a function of water vapour amount during acetylene oxidation by non-thermal plasma associated to $\text{Si}_{20}\text{Ti}_{20}$ material, UV-irradiated or not. Former values obtained with plasma and photocatalytic treatments are reminded by dot-lines.

is balanced by the modification of plasma chemistry due to high water amounts, leading to an improved CO_2 selectivity as discussed in Section 3.2. Those observations highlight the fact that higher CO_2 selectivities which are commonly reported for plasma/photocatalytic processes are mainly due to a photocatalytic effect under dry air, corresponding to a higher mineralization of the VOC. The improvement of CO_2 selectivity for water vapour amounts exceeding 15,000 ppm is mainly due to the non-thermal conversion of CO into CO_2 .

4. Conclusion

The presence of water vapour in the gas stream induces strong modifications on the oxidative processes: (i) the removal of acetylene is considerably slowed down in the presence of water vapour; (ii) the mineralization of the removed compound is delayed. The influence of water vapour is already noticeable at the lowest water vapour amount. This phenomenon is related (i) to competitive reactivity between water and acetylene; (ii) to the modification of the main oxidative species.

Even if the presence of water vapour inhibits the removal of acetylene by non-thermal plasma, this inhibition is weak; it does not exceed 10.5% of inhibition in the presence of 23,000 ppm of water vapour. Moreover, the formation of carbon monoxide is clearly reduced and the selectivity of carbon dioxide is highly improved. The presence of HO^* radicals strongly improves the oxidation of carbon monoxide into carbon dioxide.

The presence of water vapour inhibits dramatically the contribution of the photocatalytic oxidative process, even into the coupling experiments. The behaviour of the plasma/photocatalysis association mainly corresponds to that of plasma: the removal rate of acetylene is reduced whereas the selectivity of carbon dioxide is markedly improved over 12,000 ppm of water vapour.

Water vapour has to be considered as a significant source of oxidizing species which can lead to a major modification of oxidation processes in comparison to dry air condition.

References

- [1] J.-M. Herrmann, *Catal. Today* 53 (1999) 115.
- [2] P. Pichat, J. Disdier, C. Hoang-Van, D. Mas, G. Goutailler, C. Gaysse, *Catal. Today* 63 (2000) 363.
- [3] D.-S. Muggli, L. Ding, *Appl. Catal. B: Environ.* 32 (2001) 181.
- [4] A. Sirisuk, C.-G. Hill, M.-A. Anderson, *Catal. Today* 54 (1999) 159.
- [5] S. Yamazaki, S. Tanaka, H. Tsukamoto, *J. Photochem. Photobiol. A: Chem.* 121 (1999) 55.
- [6] L. Cao, A. Huang, F.-J. Spiess, S.-L. Suib, *J. Catal.* 188 (1999) 88.
- [7] J. Arana, J.-M. Dona-Rodriguez, C. Garriga-i-Cabo, O. Gonzalez-Diaz, J.-A. Herrera-Melian, J. Perez-Pena, *Appl. Catal. B: Environ.* 53 (2004) 51.
- [8] C. Raillard, V. Héquet, P. Le Cloirec, J. Legrand, *J. Photochem. Photobiol. A: Chem.* 163 (2004) 425.
- [9] F. Thevenet, O. Guaitella, J.-M. Herrmann, A. Rousseau, C. Guillard, *Appl. Catal. B: Environ.* 61 (2005) 62.
- [10] T. Oda, *IEEE Trans. Ind. Appl.* 32 (1996) 227.
- [11] T. Oda, R. Yamashita, T. Takahashi, S. Masuda, *J. Electrostat.* 42 (1997) 51.
- [12] S. Futamura, A.-H. Zangh, T. Tamamoto, *J. Electrostat.* 42 (1997) 51.
- [13] F. Thevenet, O. Guaitella, E. Puzenat, J.-M. Herrmann, A. Rousseau, C. Guillard, *Catal. Today* 122 (2007) 186.
- [14] C. Ayrault, J. Barrault, N. Blin-Simiand, F. Jorand, S. Pasquiers, A. Rousseau, J.-M. Tatibouët, *Catal. Today* 89 (2004) 75.
- [15] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645.
- [16] M.A. Anderson, *Langmuir* 12 (1996) 5093.
- [17] P.A. Connor, K.D. Dobson, A.J. McQuillan, *Langmuir* 11 (1995) 4193.
- [18] S. Sakohara, L.D. Tickner, M.A. Anderson, *J. Phys. Chem.* 96 (1992) 11086.
- [19] S. Kataoka, M.I. Tjedor-Tejedor, J.M. Coronado, M.A. Anderson, *J. Photochem. Photobiol. A: Chem.* 63 (2004) 323.
- [20] T. Guo, Z. Bai, C. Wu, T. Zhu, *Appl. Catal. B: Environ.* 79 (2008) 171.
- [21] C. Raillard, V. Héquet, P. Le Cloirec, J. Legrand, *Appl. Catal. B: Environ.* 59 (2005) 213.
- [22] S. Futamura, T. Yamamoto, *J. Electrostat.* 42 (1997) 227.
- [23] F. Liu, W. Wang, S. Wang, W. Zheng, Y. Wong, *J. Electrostat.* 65 (2007) 445.

- [24] Z. Bo, J.H. Yan, X.D. Li, Y. Chi, K.F. Cen, B.C. Cheron, Plasma Chem. Plasma Proc. 27 (2007) 546.
- [25] O. Guaitella, F. Thevenet, C. Guillard, A. Rousseau, J. Phys. D: Appl. Phys. 39 (2006) 1.
- [26] T.-C. Manley, in: Proceedings of the 84th General Meeting, New York, 1943.
- [27] Z. Falkenstein, J.-J. Coogan, J. Phys. D: Appl. Phys. 30 (1997) 817.
- [28] O. Guaitella, F. Thevenet, E. Puzenat, C. Guillard, A. Rousseau, Appl. Catal. B: Environ. 89 (2008) 296.
- [29] A. Ogata, D. Ito, K. Mizuno, S. Kushiya, A. Gal, T. Yamamoto, Appl. Catal. A: Gen. 236 (2002) 9.
- [30] R. Rudolph, K.P. Francke, H. Miessner, Plasma Polym. 8 (2003) 153.
- [31] B. Ohtani, S.W. Zhang, T. Ogita, S. Nishimoto, T. Kagiya, J. Photochem. Photobiol. A: Chem. 71 (1993) 195.
- [32] P. Pichat, J. Disdier, C. Hoang-Van, D. Mas, G. Goutailler, C. Geysse, Catal. Today 63 (2000) 363.